

(NASA-CR-196580 GROWTH OF SINGLE
CRYSTALS OF ORGANIC SALTS WITH
LARGE SECOND-ORDER OPTICAL
NONLINEARITIES BY SOLUTION
PROCESSES FOR DEVICES Final Report
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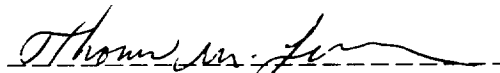
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GROWTH OF SINGLE CRYSTALS OF ORGANIC SALTS
WITH LARGE SECOND-ORDER OPTICAL NONLINEARITIES
BY SOLUTION PROCESSES FOR DEVICES

Final Report for Contract NAS8-38609
Delivery Order No. 93

by

The University of Alabama in Huntsville


Thomas M. Leslie PI



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INTRODUCTION

This delivery order has several parts and tasks that needed to be fulfilled. these were

a. Data obtained from the EFISH and Kurtz Powder Methods will be will be provided to Moore and Cardelino (MSFC) for further refinement of their method. They are working on a theoretical model for predicting the second-order nonlinearities of organic salts. These data will aid in the molecular engineering and screening of new NLO salts. A number of MSFC supplied materials have also been tested and these data can be found in the portion of the document written by Dr. Mohan Sanghadasha.

b. A number of salts will be synthesized with various counterions. With the previous literature as a guide, several salts with promising SHG activities and new salts will be tested for the presence of two crystalline forms. The materials will be recrystallized from dry and wet solvents and compared for SHG efficiency. Salts that have a high SHG efficiency and no tendency to form hydrates will be documented. This can be found in the portion of the document written by Mr. Wang and Dr. Leslie. Materials have been supplied and are available for further study. The synthesis of these materials are included in this report.

c. Methods will be investigated to aid in the growth of large, high quality single crystals by solution processes. These crystals will be characterized for their applicability in the fabrication of devices that will be incorporated into optical computers in future programs. Single crystals of optimum quality may be obtained by crystal growth in low-gravity. This can be found in the portion of the document written by Dr. Maria Zugrav.

d. We will start the design of a temperature lowering single crystal growth apparatus for ground based work. At least one prototype will be built. Dr. Zugrav was not able to complete this portion of the contract. Her time was spent obtaining the results mentioned in this report along with obtaining DAST seed crystals from solution using a variety of solvents. The funds allocated for the materials needed to build a crystallizer have been returned.

EFISH Experiments: Sanghadasa

A third-order process known as the electric field induced second harmonic generation (EFISH) is often used to determine the second-order coefficient, β , of non-centrosymmetric molecules and the third-order coefficient, γ , of centrosymmetric molecules in the liquid phase. In this method, a non-phase matched second harmonic (SH) is generated by mixing the dynamic field with the static field which is applied to align the dipoles and create a non-centrosymmetric

arrangement of molecules. The SH intensity is measured as a function of interaction length and the resulting fringe pattern, along with some other measurements, are then used to determine the molecular nonlinearity.[1,2]

However, several types of inaccuracies and incompatibilities of EFISH measurements have appeared in the literature.[3] The inappropriate design of the experimental setup itself, especially the liquid cell, and the ignoring of the imaginary part of the nonlinearity when the frequency associated with the molecular excited state is near the second harmonic wavelength [4] can be identified as two major reasons for the inconsistencies. In this project, a new version of the EFISH experiment was performed. The experiment was designed so that it did not possess the drawbacks of the conventional EFISH experimental setup. An entirely new type of liquid cell was designed and the experiment was performed in two different stages to determine the coherence length and the absolute value of the second-order microscopic susceptibility.

Since many sources of error in the conventional EFISH experiment have been attributed to the design of the liquid cell, designing a new cell was the priority in the second stage of the experiment. One of the major differences in the process of second harmonic generation in the cell was the orientations of electric fields. In the standard EFISH cell, both the static and dynamic electric fields were perpendicular to the plane of incidence. However, in the new design, the D.C. electric field was in the plane of incidence and the fundamental beam had to be polarized parallel to the plane of incidence to achieve second harmonic generation.

The new liquid cell consists of two pieces of indium tin oxide (ITO) coated, conductive, transparent glass windows, of good optical quality and a 1.5 mm thick flat glass spacer. The ITO coated glass plays the roles of both window and electrode. A 12 mm diameter hole and a 1 mm deep groove are made in the middle of the spacer and it is sandwiched between the windows using silicone rubber adhesive which had been proven to be solvent resistant. The resulting disk shaped cavity defined the volume of the liquid sample. The assembly of the cell was done precisely, with the aid of a He-Ne laser so that the two windows were parallel to each other. The conductive layer of each window was on the internal surface, hence the D.C. electric field, E_0 , exists only in the

liquid. The windows are longer than the glass plate between them so that they extend away from the cell to avoid any arcing across the electrodes. Before these parts are assembled, the conductive areas near the edges of the glass have been removed to avoid arcing. The groove on the spacer forms a tiny hole through which the liquid sample is injected into the cell using a hypodermic syringe and a needle. A quartz crystal sandwiched between two pieces of similar conductive glass using index matching liquid is placed on top of the cell. The cell is mounted at the center of a computer controlled positioning system consisting of a rotational stage with a vertical axis of rotation and two translational stages with motion in horizontal and vertical directions. The resolution of the rotational stage is 0.001° and that of the translational stage was $1\text{ }\mu\text{m}$.

A Q-switched Nd:YAG laser (Quanta Ray DCR-11 with near-Gaussian optics) with a fundamental wavelength of 1064 nm operating at a repetition rate of 10 Hz was used in the experiments. The duration of a single laser pulse was about 10 ns. A half wave plate and polarizing beamsplitter were used to obtain a horizontally polarized beam and also to control the intensity. An adequately clean beam with sufficient energy (about 3-5 mJ) was obtained by spatially filtering the beam with the aid of a diamond pin hole and nearly collimating it with a short focal length lens (10 cm). The beam was focused in the region where the liquid cell was located, with the aid of a long focal length lens (110 cm). The short focal length lens was mounted on a X-Y-Z translational stage with a resolution of $10\text{ }\mu\text{m}$ so that the size and the position of the beam in the cell could be controlled precisely.

A combination of positive lenses was used so that the divergence of the beam could be finely adjusted. The rest of the experimental set up, except for a few items, was isolated from the flashlamp light of the laser and room light by using dark boxes with both input and output openings covered with long pass color glass filters. A small fraction of the laser beam was reflected by a quartz window to generate a second harmonic signal from a standard cut KDP crystal and the signal used to monitor intensity fluctuations of the fundamental laser beam. A set of filters, including a highly concentrated CuSO_4 solution, a broad band filter, a linear polarizer, neutral density filters and a narrow band interference filter (532 nm) were employed to isolate the

SH beam from the residual fundamental IR beam. The SH beam is then detected by a high gain PMT. The IR laser beam is focused into the liquid cell and the rest of the optical alignment is performed with the aid of a He-Ne laser beam which propagates along the path of the infrared beam. The shape of the output pulse from the PMTs is improved by using a snubber network. Output signals from the PMTs are amplified by fast pre-amplifiers before being sent to a computer through gated integrator and boxcar averagers (GIBA). The outputs of the GIBAs are stored in the computer. In addition to GIBAs, the computer also controls the laser, H.V pulse generator and the drivers for the translational and rotational stages.

Since both dynamic and static fields must be parallel to each other in order to generate second harmonic from the liquid, the liquid cell had to be turned so that it formed a non-zero angle of incidence. The knowledge of the angle of incidence was very important in this experiment and therefore it was measured very accurately. A 45° angle of incidence was used in the experiment. In this experiment, the optical path length was changed by rotating the sample instead of translating the cell. The reference quartz crystal was also rotated to generate a Maker fringe patterns. A rectangular shaped crystal was required instead of the wedge shaped one used in the standard EFISH experiment.

By firing the laser pulses when the high voltage pulses were on, second harmonic could be generated. The cell was rotated by small steps of 1.5 m rad , from 45° to 50° , and the corresponding second harmonic intensity was measured. Once all the data were collected, the cell was returned to its original position. Then, the translational stage with the vertical motion moved the cell downward, bringing the quartz crystal mounted on top of the cell into the path of the laser beam. At that time, more neutral density filters had to added in order to attenuate the stronger second harmonic generated by the crystal and the linear polarizer had to be turned by 90° . The cell was then rotated and the data were collected in the same manner as with the liquid cell. Once data collection was finished, the crystal was turned back to its original position, and then the translational stage moved it upward, bringing the EFISH cell back into the laser beam. Then, the stage was turned by an angle of twice the initial angle of incidence keeping the same front surface

towards the input beam and the data collection procedure was repeated. After all data were taken, the sample was withdrawn from the cell and the cell flushed with the solvent several times. Then, the cell was ready for another sample.

The intensity of the second harmonic generated by the cell can be expressed in the following form:

$$I_{2\omega}(\theta) = AF_1F_2F(\theta)(\sin^2 \varphi'(\theta) + \sinh^2 \varphi''(\theta)) \quad (1)$$

where

$$A = \frac{c}{8\pi} \left[\frac{16\pi\chi^{(3)}E_0E_\omega^2}{[n_2]^2([n_2]^2 - [n_1]^2)} \right]^2 \quad (2)$$

$$F_1 = \frac{[t_1^{(1)}t_1^{(2)}]^4}{D^2} \quad (3)$$

$$D = n_2c_2^{glass} + n_2^{glass}c_2 \quad (4)$$

$$F_2(\theta) = \frac{1}{64}(2\sin 2\theta - \cos 4\theta)^2 \left[\frac{e^{-2\varphi''}}{1 + [\frac{\varphi''}{\varphi}]^2} \right] \quad (5)$$

$$\varphi' = \frac{\pi L}{2l_c(\theta)} \quad (6)$$

and

$$\varphi'' = \frac{L\alpha_2}{2c_2} \quad (7)$$

The quantity $l_c(\theta)$ is given by

$$l_c(\theta) = \frac{\lambda}{4[n_2c_2 - n_1c_1]} \quad (8)$$

The variation of the term F_1 within the angular range from 45° to 50° is negligible and, therefore, it was assumed to be constant in the curve fitting procedure. L is the thickness of the cell and θ is the angle of incidence. The quantity φ'' which depends on the absorption coefficient α was ignored for materials characterized in this project. In Eqs. (1)-(8) the subscripts 1 and 2 refer to the fundamental and second harmonic beams respectively and c and s define the sines and cosine

functions. $t^{(1)}$ and $t^{(2)}$ are transmission coefficients for the transmission of light from air to glass and glass to liquid respectively.

Since the coherence length of each sample was measured using another experimental setup which was in the form of a nonlinear interferometer, the values of indices of refraction at both wavelengths were known. By measuring the average intensity of the second harmonic the macroscopic susceptibility $\chi^{(3)}$ is determined. Then, the second-order microscopic susceptibility β of the solute can be determined from the relation

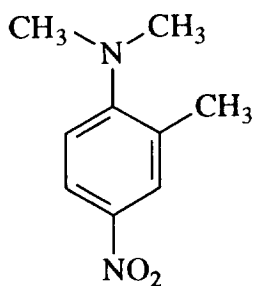
$$\chi^{(3)}(-2\omega; \omega, \omega, 0) = N f_{2\omega} f_{\omega}^2 f_o \bar{\gamma} \quad (9)$$

where

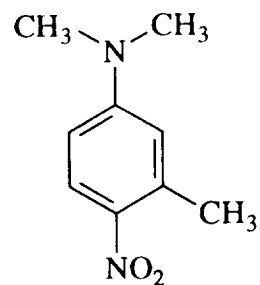
$$\bar{\gamma} = \gamma + \frac{\mu\beta}{5KT} \quad (10)$$

f_{ω} is the local field factor, at the frequency ω , which relates local electric field to the external electric field. However, the infinite dilution extrapolation technique has to be used to minimize the solute-solute interactions and, in particular in polar solvents, the solvent-solvent interactions due to hindered rotation. Using experimental values of dielectric constant ϵ , index of refraction n and macroscopic susceptibility $\chi^{(3)}$ at various concentrations, the slopes of each of them at infinite dilution, i.e. $\left[\frac{\partial\epsilon}{\partial C}\right]_v$, $\left[\frac{\partial n}{\partial C}\right]_v$ and $\left[\frac{\partial\chi^{(3)}}{\partial C}\right]_v$ can be obtained. Hence, β is determined.[3]

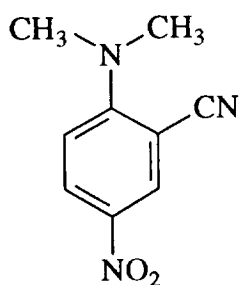
The following materials shown the experimental β values were characterized in this project. All materials were dissolved in anhydrous 1,4-dioxane. Concentrations in the range between 0.01 M to 0.5 M were used depending on their solubility. The uncertainty of the value of β of all materials, except (4) and (9), was less than 3%.



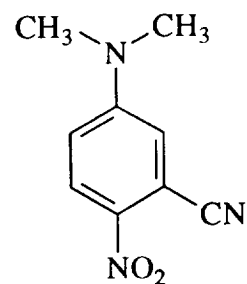
(1) BETA = 24.5×10^{-30} esu



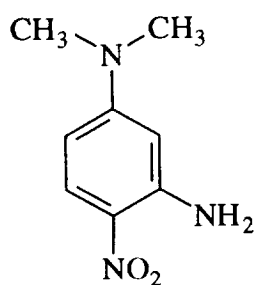
(2) BETA = 22.8×10^{-30} esu



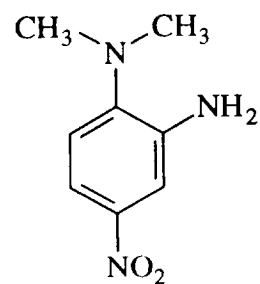
(3) BETA = 22.5×10^{-30} esu



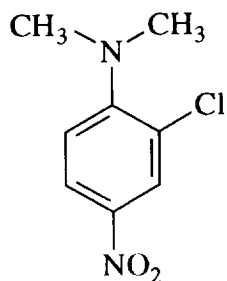
(4) BETA = 23.2×10^{-30} esu



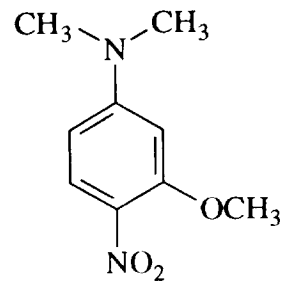
(5) BETA = 21.8×10^{-30} esu



(6) BETA = 20.2×10^{-30} esu



(7) BETA = 24.5×10^{-30} esu



(8) BETA = 25.3×10^{-30} esu

References

- [1.] K.D. Singer and A.F. Garito, "Measurements of molecular second order optical susceptibilities using dc induced second harmonic generation," J. Chem. Phys. 75, 3572 (1981).
- [2.] C.C. Teng and A.F. Garito, "Dispersion of the nonlinear second-order optical susceptibility of organic systems," Phys. Rev. B 28, 6766 (1983).
- [3.] K.D. Singer, J.E. Sohn, L.A. King, H.M. Gordon, H.E. Katz, and C.W. Dirk, "Second-order nonlinear-optical properties of donor- and acceptor-substituted aromatic compounds," J. Opt. Soc. Am. B 6, 1339 (1989).
- [4.] C.G. Bethea, "Experimental technique of dc induced SHG in liquids: measurement of the nonlinearity of $\chi^{(2)}$," Appl. Opt., 14, 1447 (1975).

Synthesis of Materials: Wang and Leslie

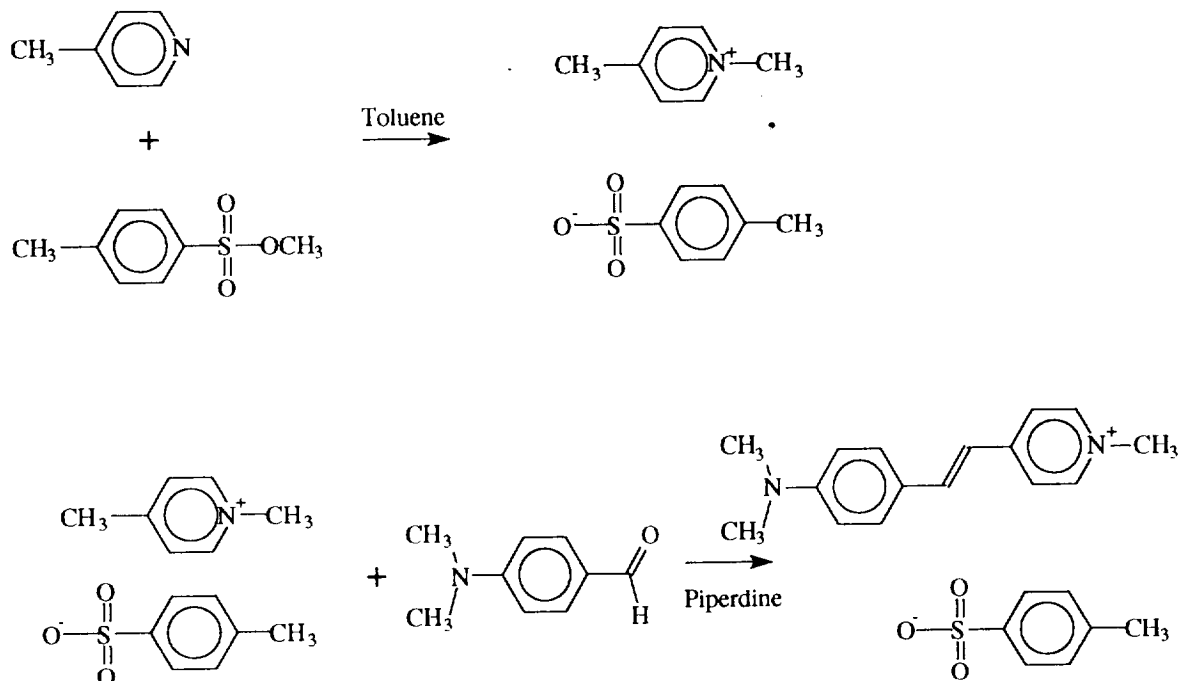
The literature prep of DAST was used to produce the large quantities of DAST required for these studies. This method is included below under the title "4-N,N-dimethylaminostyryl pyridinium tosylate (DAST)". This method is not suitable for rapid modifications of the structure and each new compound would require a new synthetic procedure. Therefore, we thought if the styryl pyridine could be synthesized by a different synthetic procedure, flexibility would be added to the project. DAST was indeed synthesized by an alternate route that allows for more flexibility in the synthetic scheme. The DAST styryl pyridine precursor can be synthesized by the (proprietary) route shown below and reacted with methyl p-toluenesulfonate in a S_N2 displacement reaction. The flexibility of the procedure is shown by the styryl pyridine's reaction with 1,3-propane sultone to make the covalently attached zwitterionic compound.

4-N,N-dimethylaminostyryl pyridinium tosylate (DAST)

4-picoline (9.3 g, 0.1 mole) is weighed out and added to 200 mL of toluene in a 500 mL round bottom flask. Then methyl tosylate (18.6 g, 0.1 mole) is slowly added to the flask. The mixture is heated gently to form a salt which is insoluble in toluene. The mixture is heated to boiling and then just enough DMF was added to get the salt into solution. 4-N,N-dimethylaminobenzaldehyde (14.9 g, 0.1 mole) was weighed out and added to the flask. A few drops of piperidine was added as catalyst until the solution turns to red. The mixture was heated at reflux for two days, and the resultant water was taken off in a Dean-Stark trap at the same time.

When no more water came out, the mixture was cooled down to room temperature. Red crystals were collected and air dried, and then recrystallized from dry methanol. The resultant crystals were purple in color, m.p. 256-258 °C. This is the non-hydrate form.

The hydrate form was prepared by recrystallization of the above material from water. The crystals obtained were larger in size and orange-red in color. The hydrate has roughly the same melting point as the nonhydrate material. All observations were conducted using a Nikon Polarizing microscope fitted with a Mettler FP-52 hot stage. The difference is, when the hydrate is subjected to melting, it dehydrates between the temperatures of about 125-145 °C. It is not possible to tell exactly when the material changes from the hydrate to the anhydrous form since there is an obvious cracking of the crystals and morphology change over this entire temperature range. One then obtains the melting point of the anhydrous material. Upon cooling and re-melting, a slightly broader melting range of 252-256 °C is obtained.

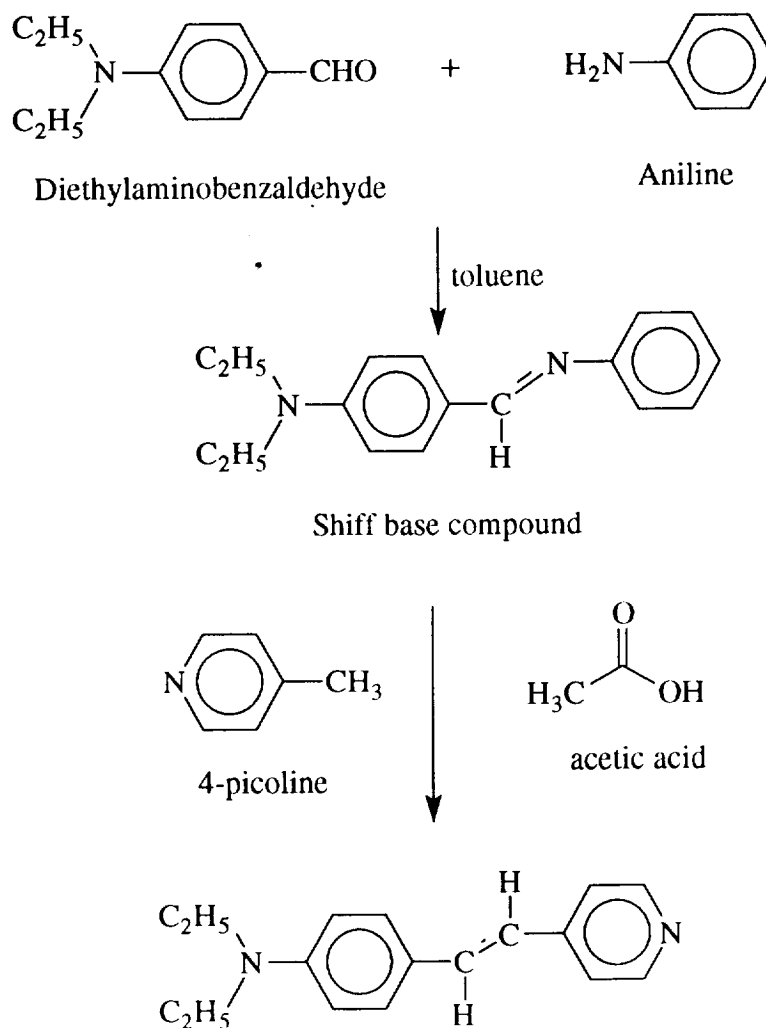


Synthesis Procedure for Dimethylaminostyryl Pyridine (DMASP)

Schiff's Base: In a 500 mL RB flask, dimethylaminobenzaldehyde (29.8 g, 0.2 mole) and aniline (18.2 g, 0.2 mole) were dissolved in 250 mL of toluene. One drop of toluene sulfonic acid was added as catalyst. The flask fitted with a Dean-Stark water trap was then heated at reflux with stirring overnight. Theoretical amount of water was collected in the trap. The flask was allowed to cool. The toluene was removed on the rotovap. The resulting solid was then recrystallized from

2-propanol. Yellow crystals were obtained, m.p. 93.7-95.3 °C.

Dimethylaminostyryl Pyridine: The above Schiff's base (about 0.2 mole) was dissolved in 150 mL of glacial acetic acid. The solution was orange to red in color. 4-picoline (18.6 g, 0.2 mole) was added to the solution. The resultant solution was then heated at reflux for about 8 hours. The solution was cooled to room temperature and then poured into about 400 mL of water in a beaker. A concentrated ammonium hydroxide was slowly added in small portion until the solution was no longer acidic. The resultant solid was collected and washed with deionized water. The solid was then recrystallized twice from chlorobenzene. Nice yellow crystals were obtained, m.p. 242.6-244.0 °C.



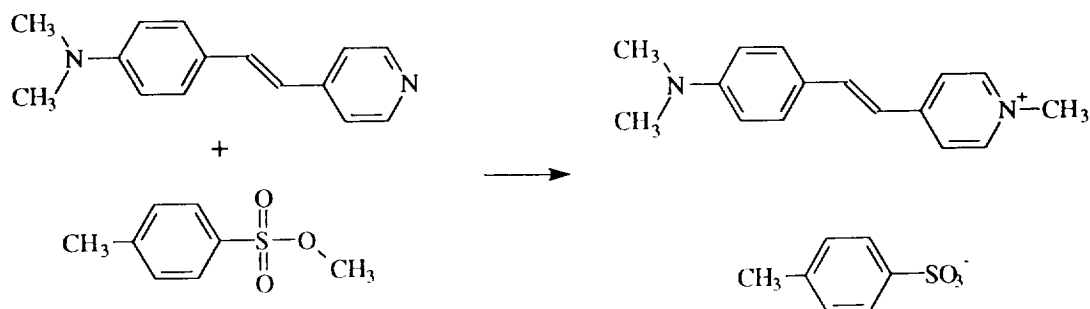
Synthesis Procedure for 4-Hydroxystyryl Pyridine (HSP)

Schiff's Base: The procedure was exactly as above but with 0.02 mole of 4-hydroxy benzaldehyde substituted for the 4-N,N-dimethylaminobenzaldehyde. The slightly off white hydroxy Schiff's base is recrystallized from toluene and melts at 194-196 °C.

4-Hydroxystyryl Pyridine (HSP) The procedure was exactly as above but with the Schiff's base from the reaction with hydroxy benzaldehyde substituted for the Schiff's base made from 4-N,N-dimethylaminobenzaldehyde. The acetic acid reaction solution is bright yellow instead of dark red. The pale cream colored solid can also be recrystallized from chlorobenzene to yield crystals melting from 196-199 °C.

4-N,N-Dimethylaminostyryl Pyridinium Tosylate (DAST) Alternate

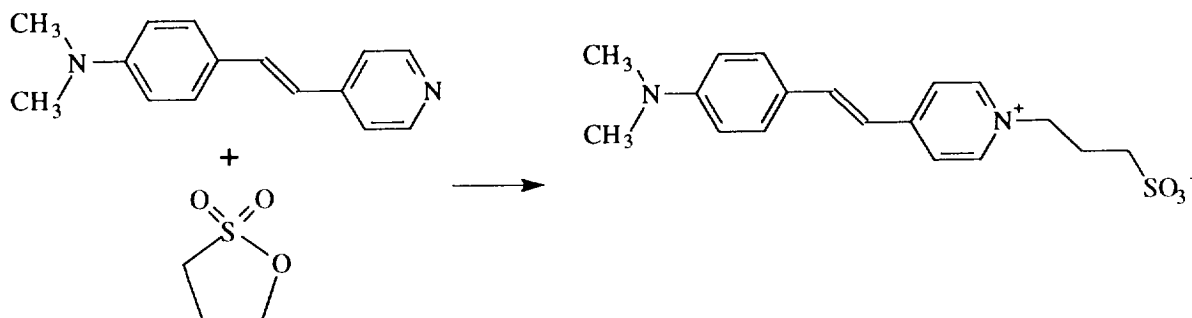
Dimethylaminostyryl Pyridinium Tosylate: Dimethylaminostyrylpyridine (4.48 g, 0.02 mole) was weighed into about 80 mL of chlorobenzene in a 250 mL round bottom flask fitted with a magnetic stir bar. The mixture was gently heated (about 75 °C) with stirring until all the solid dissolved. Methyl p-Toluene Sulfonate (3.72 g, 0.02 mole) was then added to the warm stirring solution. A dark purple-red precipitate was formed. The mixture was gently heated for two more hours and cooled down to crystallize. About 6.5 g of tiny metallic green-red crystals were obtained, m.p. 253-257 °C. The crystals were collected, air dried, and then recrystallized from dry methanol. The resultant crystals were purple in color, m.p. 256-258 °C.



4-N,N-Dimethylaminostyryl Pyridinium Tosylate Propanesulfonate

Dimethylaminostyryl Pyridinium Propanesulfonate: Dimethylaminostyrylpyridine (4.48 g, 0.02

mole) was weighed into about 80 mL of chlorobenzene in a 250 mL round bottom flask fitted with a magnetic stir bar. The mixture was gently heated (about 75 °C) with stirring until all the solid dissolved. 1,3-Propane sultone (2.44 g, 0.02 mole) was then added to the solution. A red precipitate was formed. The mixture was heated for two more hours and cooled down in order to allow the product to crystallize. About 6 g of tiny red crystals were obtained, m.p. 301-304 °C. The product was not further purified.



GROWTH OF DAST CRYSTALS FROM SOLUTION: **Zugrav**

In order to investigate the crystalline habit of DAST (dimethylamino styryl pyridine), several solvents, in pure form, were tried. Commonly, DAST can be dissolved in most of the polar organic solvents, e.g. alcohols, acetone, dimethyl sulfoxide as well as water. The choice of solvent was limited by the fact that DAST has two forms, anhydrous and hydrate, and only the anhydrous form is the one that gives the large second order nonlinear optical activity. This limits the choice to only anhydrous solvents that can be kept dry. Preferably, the solvent itself is not miscible with water nor hygroscopic. This eliminates very good recrystallization solvents such as methanol.

There have been several attributes considered for selecting the solvent ability: the compatibility of the solvent with DAST, the solubility, the thermal stability, the physiological properties. Among the different solvents tested, nitromethane and acetonitrile gave the best results. A combination of the classical growth methods, cooling and evaporation, were used to get first nuclei by the spontaneous nucleation and then to grow them into seed crystals. Seed crystals of

DAST were prepared from nitromethane or acetonitrile solutions by cooling a warm saturated solution or by allowing a saturated solution to evaporate very slowly at room temperature. These solutions were placed in 25 cm³ conical flasks covered with perforated parafilm. The resulting specimens were typically grown in four to six weeks.

In solution growth, DAST shows different crystal habits from solution to solution. Seed crystals grown from nitromethane and acetonitrile exhibit different morphologies. Solution growth from nitromethane by solvent evaporation gave very finely divided bladed crystals up to 12 mm in length, and 3x1 mm² in cross section as shown in Fig. 1. Growth from acetonitrile solution yields seed crystals with more isometric habits, as shown in Fig. 2.

An important observation is that the fast crystallization from nitromethane solution (e.g. rapid evaporation or cooling of concentrated solutions) favors even more strongly the formation of distinctly elongated crystals in high proportion of the total crystal mass. Under these conditions, the supersaturation is high and a large number of small crystals is formed initially by homogeneous nucleation. Convective mixing, due to density differences, which reduces the thickness of the diffusion barrier at the crystal-solvent interface would be much more intense than in slow crystallization.

The formation of different habits from different solvents can be explained by stereospecific solute-solvent interactions or by surface entropy factor (α) theory [1, 2]. The α theory predicts that α will decrease with increasing solubility. Thus, when a substance crystallizes from different solvents, high solubilities will lead to low α and increased growth rates. The magnitude of α indicates the "roughness" of the crystal-solvent interface, and thus the ease with which the crystal grows. When the growth surface is "rough", the crystal can grow by surface nucleation at any supersaturation. When the surface is "smooth", crystal growth is possible at low supersaturation only if screw dislocations are available.

There is a noticeable difference in DAST solubility between the two solvents, with solubility increasing with temperature. Compared with DAST solubility in acetonitrile solvent, the DAST solubility in nitromethane solvent was more temperature dependent and therefore more

appropriate to grow DAST crystals by the method of temperature reduction.

It is worth noting that the supersaturated solutions of DAST in nitromethane had a larger width of the metastable zone . This is a great advantage and a good starting point for the growth from solution of large single crystals of DAST .

Conclusions and future work

Surprisingly, the simplest method of growing an organic single crystal by dissolving the material in a solvent, and then allow the solvent to evaporate slowly, has been worked well for DAST yielding optically clear specimens with macroscopic single crystallinity.

The future work (in the time frame of another contract) is to pursue solution growth by isothermal evaporation. The slow evaporation of the solvent can be accomplished by placing a beaker with the solution into a vacuum-desiccator and letting a dry inert gas stream such as nitrogen pass through the desiccator under well controlled flow and constant ambient temperature conditions. An external surrounding large volume water jacket is useful to stabilize against short time temperature fluctuations. Alternatively, the cooling method may be applied by using a bath which is programmed to slowly decrease in temperature. More sophisticated versions of solution growth by cooling are based on a continuous dissolution of the starting material and crystallization through solution recirculation in a two vessel crystallizer [3]. The system provides the advantages of constant temperature and precise control, flexible enough for any sort of solubility characteristics.

References

- [1]R. J. Davey, J. Crystal Growth, 76 (1986) 637.
- [2]R. J. Davey, in: Current Topics in Materials Science, Vol. 8, Ed. E. Kaldis (North-Holland, Amsterdam, 1982) pp. 431- 479.
- [3]M. Ittu Zugrav, A. Dumitrica, A. Dumitras and N. Comaniciu, Crystal Res. & Technol., 17 (1982) 475.